



Center for Advanced
Energy Studies

*A research
partnership between
Boise State University,
Idaho National
Laboratory, Idaho
State University and
University of Idaho.*

Center for Advanced Energy Studies

Electrochemical Zirconium Recovery Experiments in Molten Salt System

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Outline

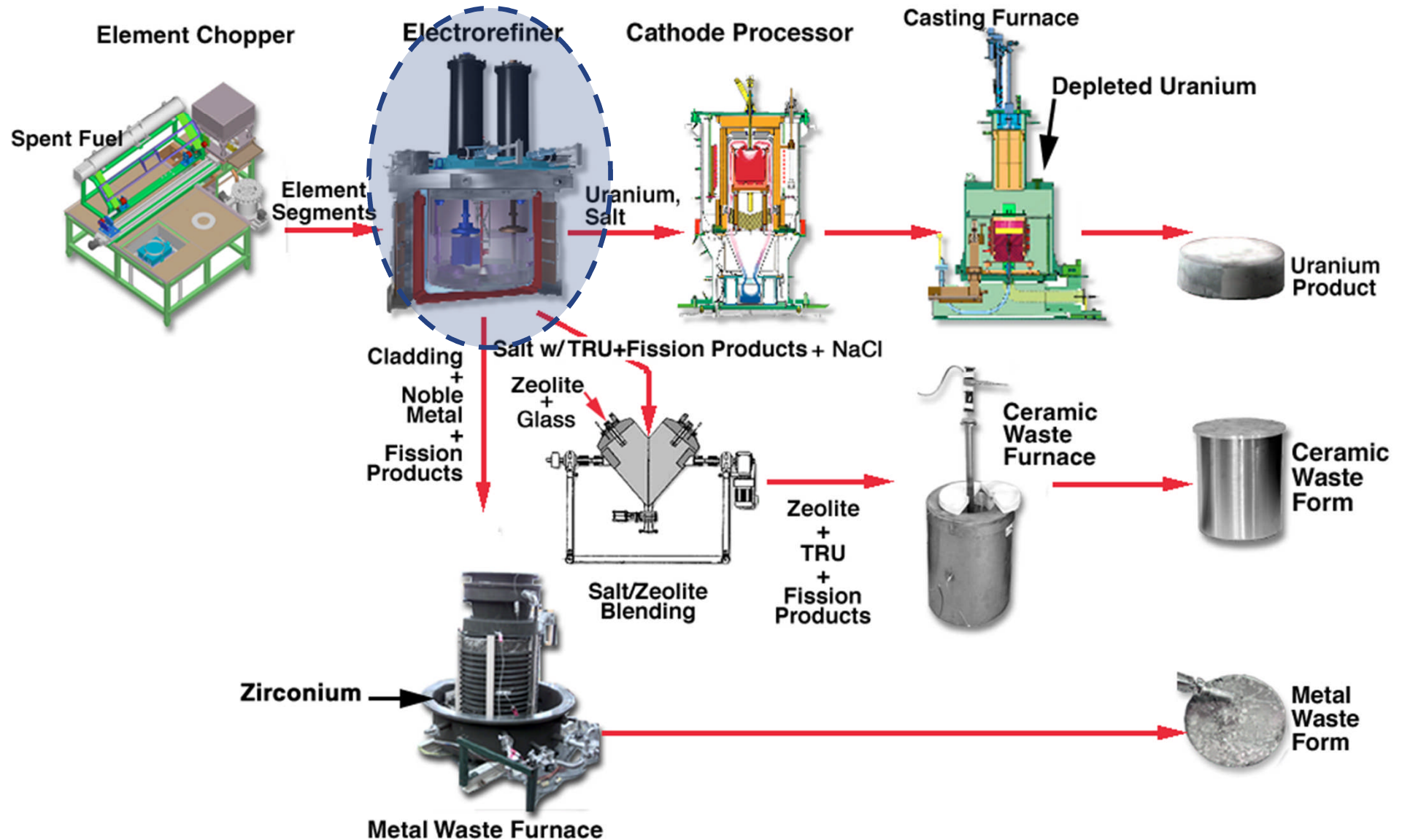
- Introduction
- Motivation and Goal
- Experimental Setup
- Experimental Procedures
- Summary & Future Work

Introduction

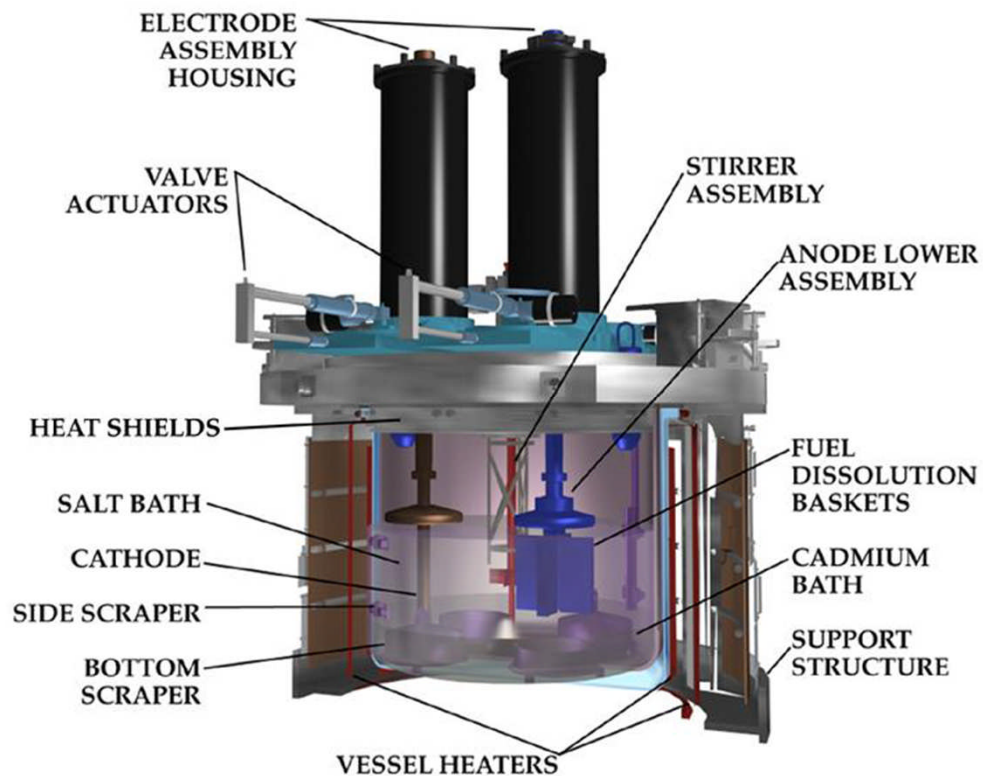
- The Experimental Breeder Reactor-II (EBR-II) was a metallic fueled, sodium cooled fast reactor operated at Argonne National Laboratory-West (currently Idaho National Laboratory) from 1963-1994.
- This reactor was fueled with a sodium-bonded, uranium-zirconium alloy fuel.
- An electrochemical process was developed by Argonne National Laboratory to treat this stainless steel clad driver fuel.
- This electrochemical process is currently being used at Idaho National Laboratory to treat the used EBR-II driver fuel.

Element	Weight % ¹	Ion
U	80.596	III
Zr	10.805	IV
Na	2.160	I
Nd	0.930	III
Mo	0.771	III

EBR-II Used Fuel Treatment Process



Mark-IV Electrorefiner (ER)

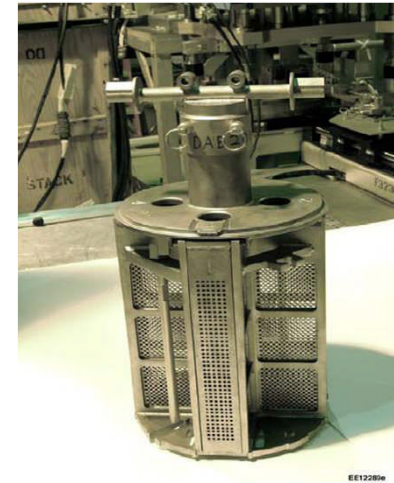


● Anode

- $U \rightarrow U^{3+} + 3e^{-}$
- $Zr \rightarrow Zr^{n+} + ne^{-}$

● Cathode

- $U^{3+} + 3e^{-} \rightarrow U$
- $Zr^{n+} + ne^{-} \rightarrow Zr$



Motivation and Goal

- Zirconium constitutes a large amount of the EBR-II used driver fuel at greater than 10 wt%.
- Over time, zirconium metal tends to build up within the Mark-IV ER and must periodically be removed.
- In developing a process to electrochemically recover pure zirconium, a knowledge of the Zr redox reactions that occur in the ER is necessary.
- To better understand this process, modeling is essential.
- In the electrochemical modeling process, there are several thermodynamic and electrochemical values that are required.
 - **Standard Reduction Potential, E^0**
 - **Diffusion Coefficient, D**
 - **Activity Coefficient, γ**

Standard Reduction Potential

- Nernst Equation:

$$E = E^0 + \frac{RT}{nF} \ln(\gamma X_s)$$

E	Equilibrium potential	n	Number of transferred electrons
E^0	Standard reduction potential	F	Faraday's constant
R	Ideal gas constant	γ	Activity coefficient
T	Absolute temperature	X_s	Mole fraction at interface

- What is the standard reduction potential, E^0 ?

- The standard potential is the equilibrium potential, E, of a given reduction reaction (i.e. $\text{Zr}^{4+} + 4e^- \rightarrow \text{Zr}$) at standard conditions.

- Pure substance at 1 atm pressure

$$- \gamma = 1 \text{ and } X_s = 1$$

- This is related to the Gibbs free energy change of the same half-cell reaction.

$$\Delta G^0 = -nFE^0$$

ΔG_i^0 Gibbs energy change of reaction i

- Mass Transfer:

$$N = kA(C_s - C_{\text{salt}})$$

$$\text{Sh} = \frac{k d_e}{\boxed{D}} = 0.0791 \left(\frac{\omega d_e^2}{\nu} \right)^{0.7} \left(\frac{\nu}{\boxed{D}} \right)^{0.356}$$

N	Molar mass transfer	C _{salt}	Bulk salt concentration
k	Mass transfer coefficient	Sh	Sherwood number
A	Total electrode surface area	d _e	Equivalent electrode diameter
C _s	Surface concentration	ω	Electrode rotation rate
		ν	Viscosity of salt

- What is the diffusion coefficient?

- Proportionality constant between molar flux and concentration gradient.

- Fick's 1st Law:

$$N = -\boxed{D} \nabla C$$

- Follows the Arrhenius temperature dependence.

$$\boxed{D} = D_0 \exp\left(\frac{-\Delta H_D}{RT}\right)$$

D₀ Pre-exponential factor
 ΔH_D Activation energy for diffusion

Available Literature Values

	Standard Reduction Potential, E^0 (V vs. Ag/AgCl)			Diffusion Coefficient, D (cm ² /s)		Activity Coefficient, γ	
	Zr(IV)/Zr	Zr(IV)/Zr(II)	Zr(II)/Zr	Zr(IV)	Zr(II)	Zr(IV)	Zr(II)
[2]	-1.22*	---	-1.12	---	---	9.6×10^{-6} *	3.4×10^7
[3]	-1.064*	-1.121*	-1.01*	---	---	---	---
[4]	-0.838	---	-0.722	---	---	3.081×10^{-3} *	1.05×10^{-4} *
[5]	-1.064*	-1.121*	-1.007*	---	---	---	---
[6]	-1.333*	---	---	---	---	---	---
[7]	-1.1	---	---	---	---	---	---
[8]	-1.22	---	---	---	---	---	---
[9]	---	---	---	---	---	4.48×10^{-3}	1.9×10^{-4}
[10]	---	---	---	1.13×10^{-5}	---	---	---
[11]				$4.53 \times 10^{-6} - 1.10 \times 10^{-7}$			

* Values reported are at 450 ° C.

[2] R. Baboian, et al., *J. Electrochem. Soc.*, **112.12** (1965).

[3] J.A. Plambeck, *J. of Chemical and Engineering Data*, **12(1)** (1967).

[4] R. Ahluwalia, et al., *Nucl. Tech.*, **126** (1999).

[5] A.J. Bard, "Encyclopedia of Electrochemistry of the Elements, Vol. X, Fused Salt Systems, p. 68, Marcel Dekker, Inc., New York (1976).

[6] M. Iizuka, et al., *J. of Nuclear Materials*, **297** (2001).

[7] T. Murakami and T. Kato, *J. Electrochem. Soc.*, **155(&)** (2008).

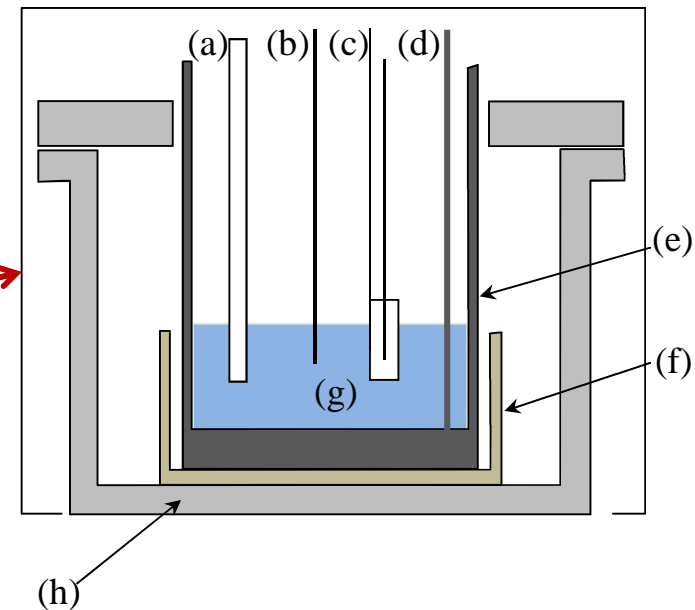
[8] A.V. Bychkov, *Proceedings of the Workshop on Pyrochemical Separations*, Avignon, France, March 14-16, 2000.

[9] R.K. Ahluwalia, et al., *Nucl. Tech.*, **133** (2001).

[10] D. Yamada, et al., *J. Alloys and Compounds*, **444-445** (2007).

[11] C.H. Lee, et al., *J. Electrochem. Soc.*, **159(8)** (2012).

Experimental Setup



- (a) Al_2O_3 sheathed thermocouple
- Monitored with Fluke 52II
- (b) Tungsten working electrode
- (c) Ag/AgCl reference electrode
(5 mol%)
- (d) Glassy carbon counter electrode
lead

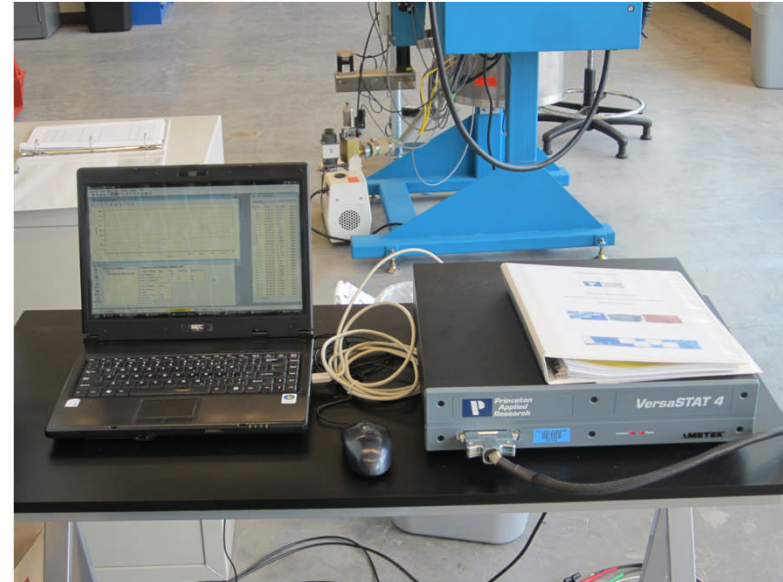
- (e) Glassy carbon crucible/counter
electrode
- (f) MgO secondary crucible
- (g) Eutectic LiCl/KCl salt containing
 ZrCl_4
- (h) Furnace
- Kerrlab with graphite crucible

Procedures

- Loading LiCl/KCl eutectic and ZrCl_4
 - (1.0, 2.5, and 5.0) wt% ZrCl_4
 - LiCl/KCl eutectic, 44/56 wt% (Sigma-Aldrich, 99.99%)
 - ZrCl_4 (Alfa Aesar, Reactor Grade, 99.5+%)
- Heating salt at 4 °C/min to 500 °C (± 2) in the salt.
- Lowering electrodes into the molten salt.
 - Tungsten Working Electrode
 - $d = 2.0$ mm (Alfa Aesar, 99.95%)
 - Glassy Carbon Counter Electrode Lead
 - $d = 3.0$ mm (HTW-Germany)
 - Ag/AgCl Reference Electrode
 - Ag wire, $d = 1.0$ mm diameter (Acros Organics, 99.9%)
 - 5 mol% AgCl in LiCl/KCl (Alfa Aesar, ultradry, 99.997%)

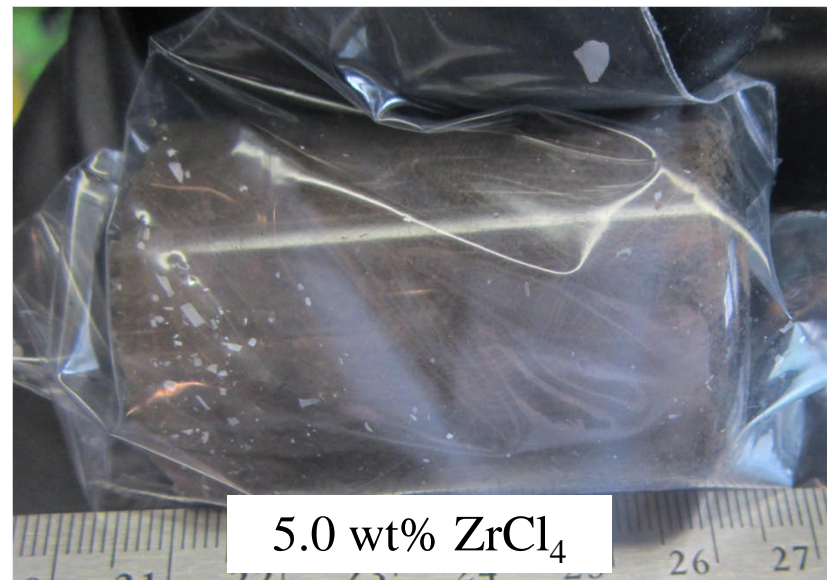
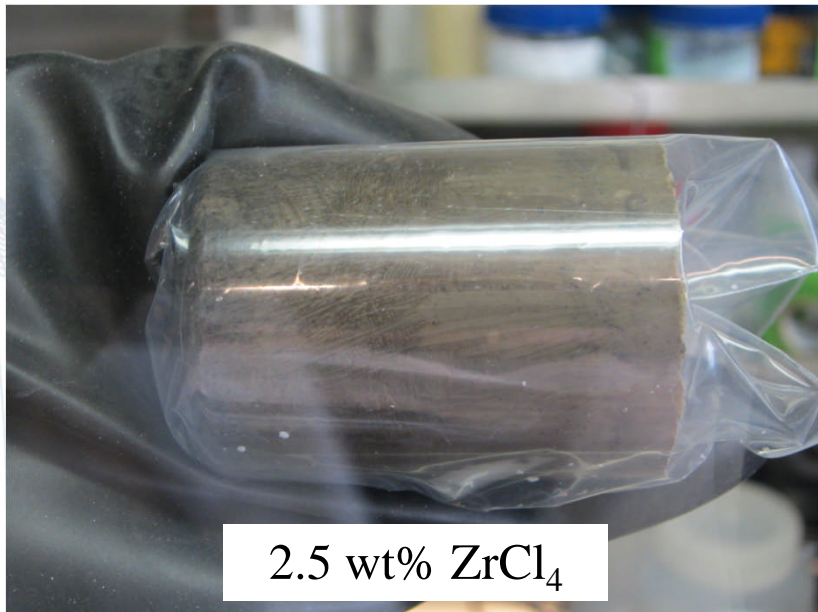
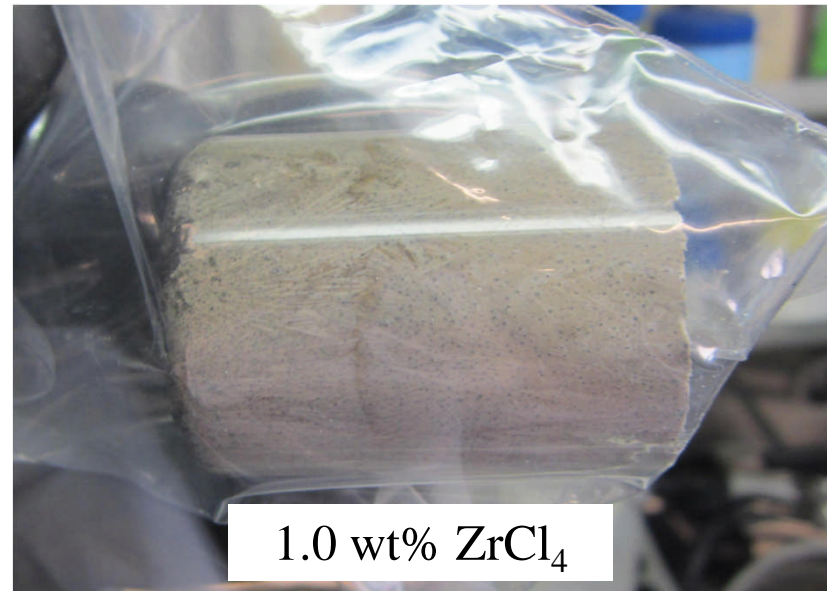
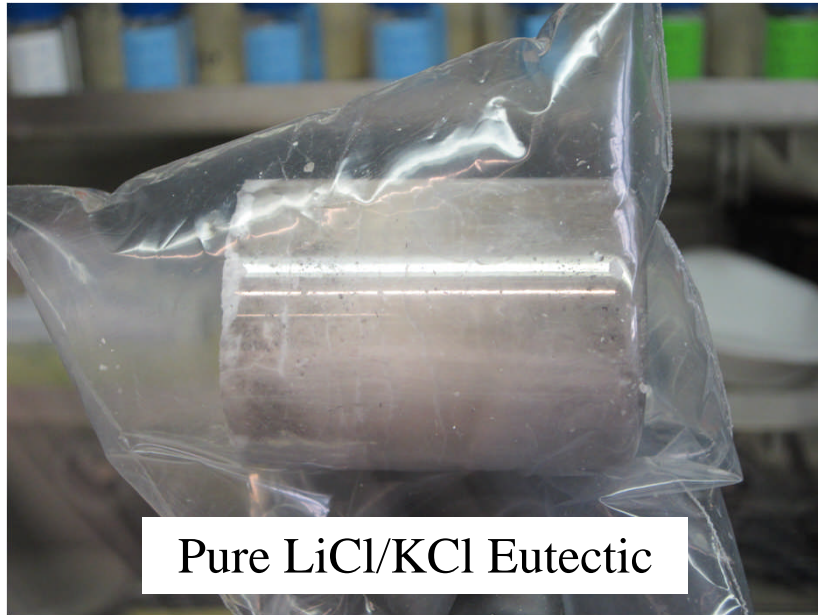


- Cyclic Voltammetry
 - Scan range: 0 V to -2.4 V
 - Scan rate: 300 mV/s to 2.0 V/s
- Chronopotentiometry
 - Driving current: 70 mA to 300 mA



- Samples taken for ICP-MS analysis.
 - Mixed:
 - 1.0 wt%
 - 2.5 wt%
 - 5.0 wt%
 - Analysis Results:
 - (0.954 ± 0.117) wt%
 - (2.49 ± 0.304) wt%
 - (4.84 ± 0.585) wt%

Chloride Salt Ingots



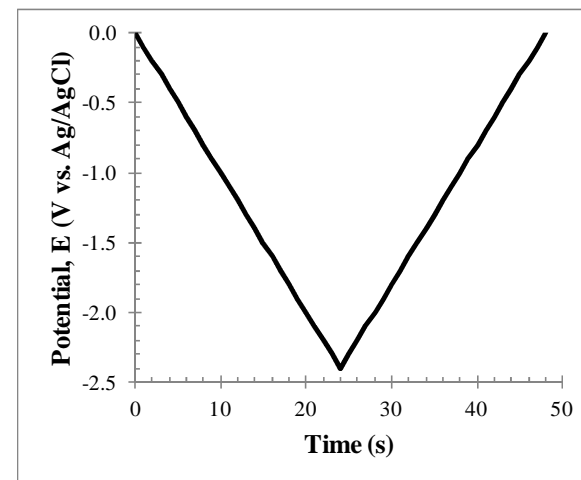
Cyclic Voltammetry (CV)

- A common electrochemical technique that can be used to determine the reactions that can occur in the electrochemical cell.
- Potential is scanned through the range of interest and current is measured.

- Potential Range Scanned: 0 V to -2.4 V

- Li⁺ Reduction: -2.561 V [12]

- Cl⁻ Oxidation: +1.065 V [12]



Potential waveform for 100 mV/s.

- From the resulting current, reaction information can be determined.

- Randles-Sevcik equation

$$\frac{I_p}{\sqrt{v}} = 0.446nFAC\sqrt{\frac{n\alpha FD}{RT}}$$

- Delahay equation

$$\frac{I_p}{\sqrt{v}} = 0.4958nFAC\sqrt{\frac{n\alpha FD}{RT}}$$

- Equilibrium potential

$$E = \frac{E_{p,a} + E_{p,c}}{2}$$

- Apparent standard potential

$$E = E^{0'} + \frac{RT}{nF} \ln(X)$$

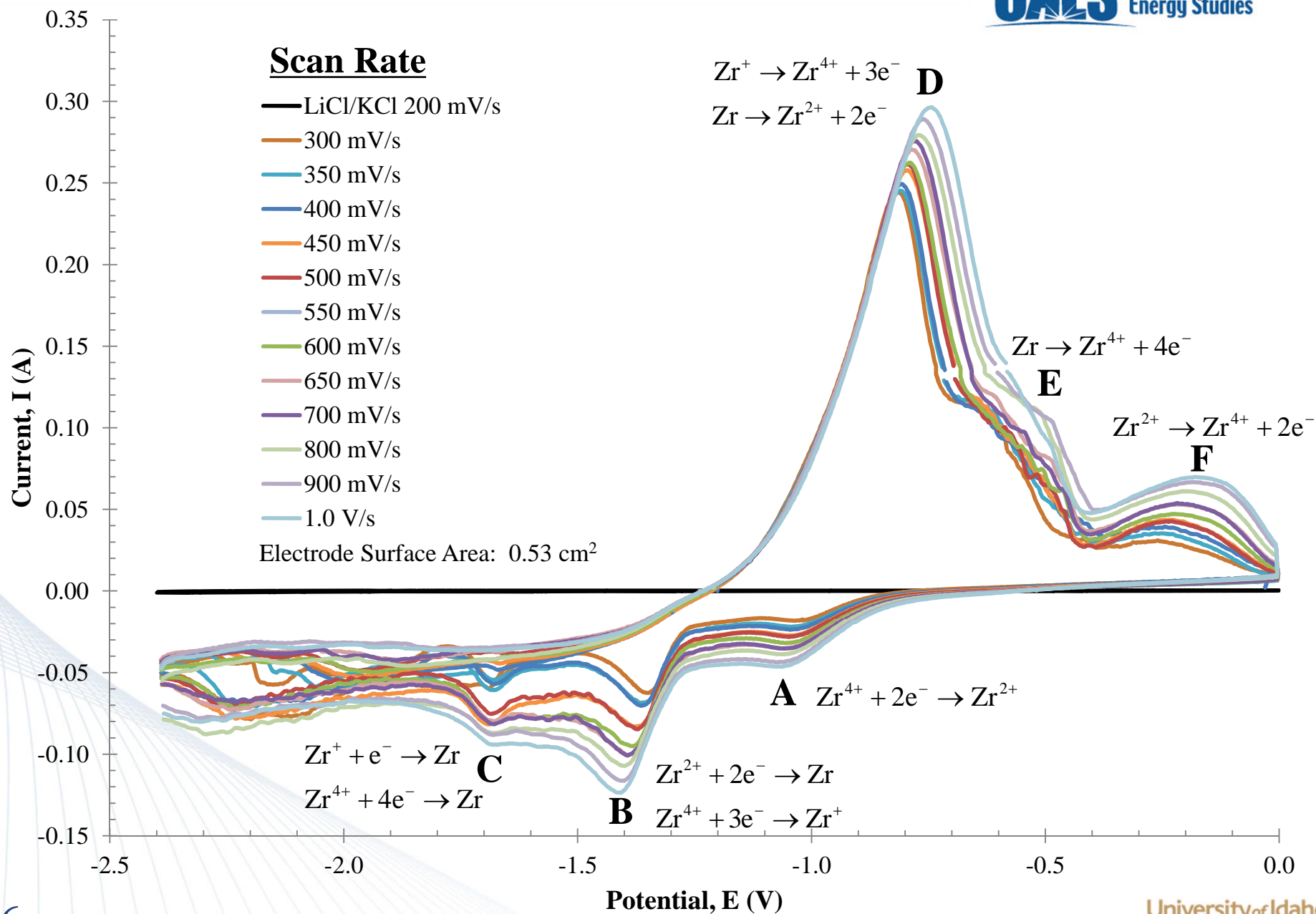
Chronopotentiometry (CP)

- An electrochemical technique that can be used to determine the diffusion coefficient of ions within the electrolyte.
- A large driving current is applied and the resulting potential is measured.
 - To maintain the applied current, the potential drops to a value at which ions of a given species are reduced.
 - When the ion is fully reduced at the electrode surface the potential drops to a potential at which the next ion will reduce.
 - This creates a plateau in the measured potential.
 - The duration of this plateau, or transition time, τ , is related to diffusion coefficient, D , through the Sand equation.

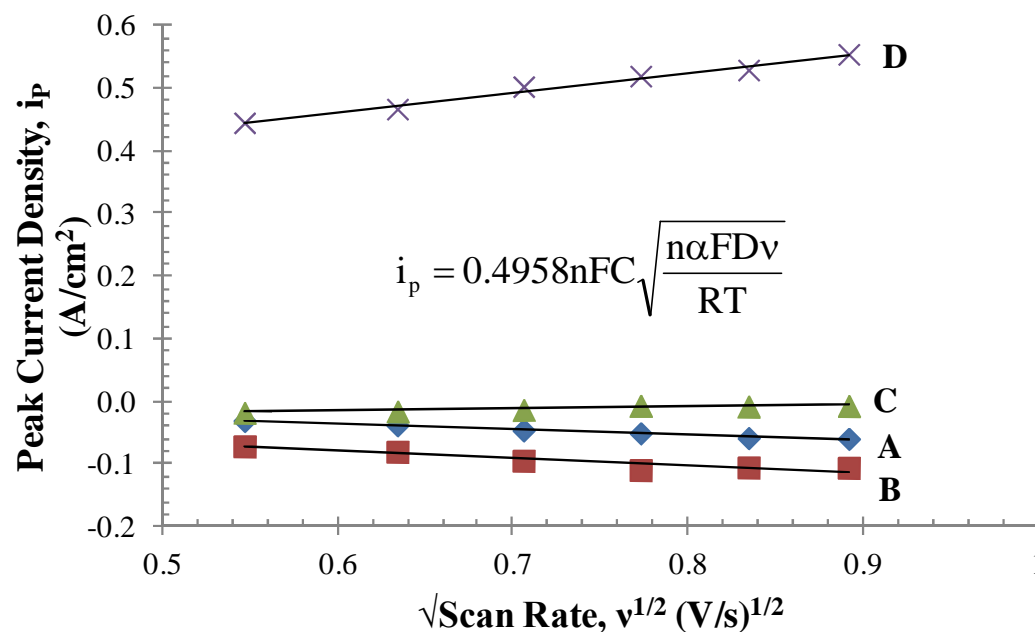
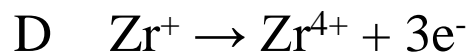
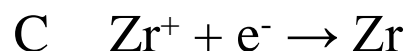
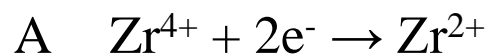
$$i\sqrt{\tau} = \frac{nFC\sqrt{\pi D}}{2}$$

- From the resulting potential response, transition time and diffusion can be determined.

Cyclic Voltammogram (1.0 wt% ZrCl_4)

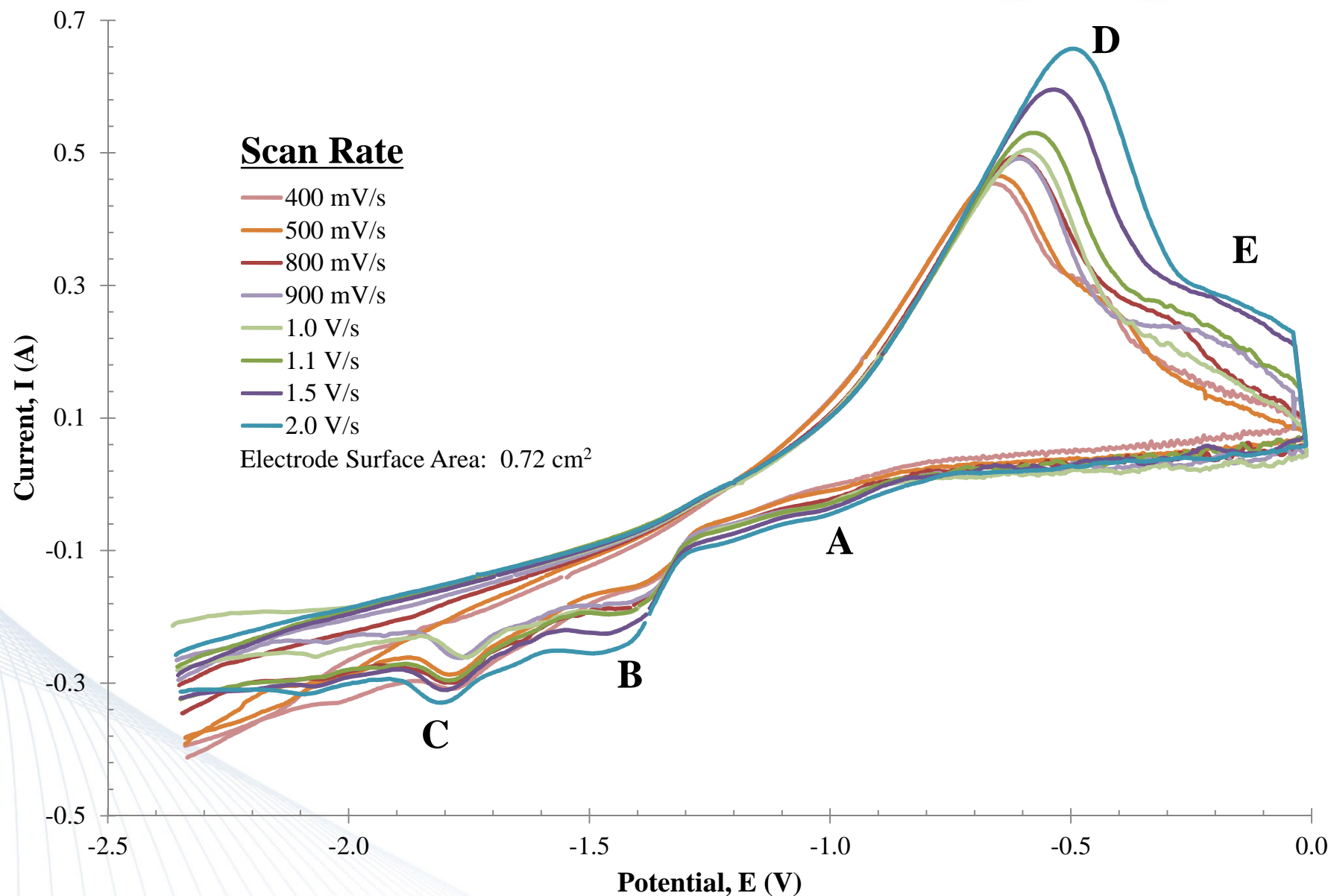


1.0 wt% ZrCl₄

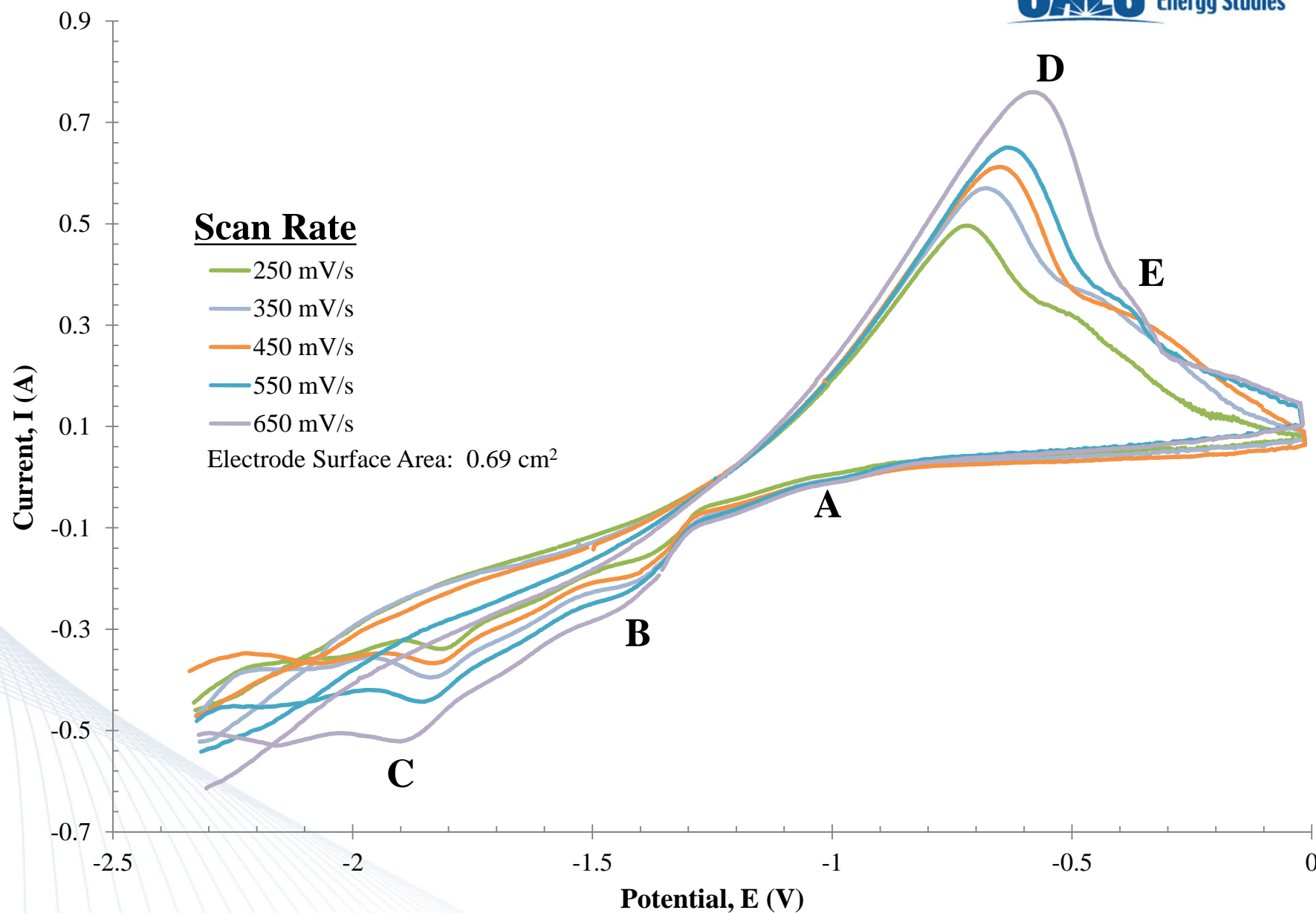


Peak	Diffusion Coefficient, D (cm ² /s)			
	n = 1	n = 2	n = 3	n = 4
A	9.26×10^{-5}	1.16×10^{-5}	3.43×10^{-6}	1.45×10^{-6}
B	1.50×10^{-4}	1.88×10^{-5}	5.57×10^{-6}	2.35×10^{-6}
C	1.52×10^{-5}	1.90×10^{-6}	5.62×10^{-7}	2.37×10^{-7}
D	1.19×10^{-3}	1.48×10^{-4}	4.39×10^{-5}	1.85×10^{-5}

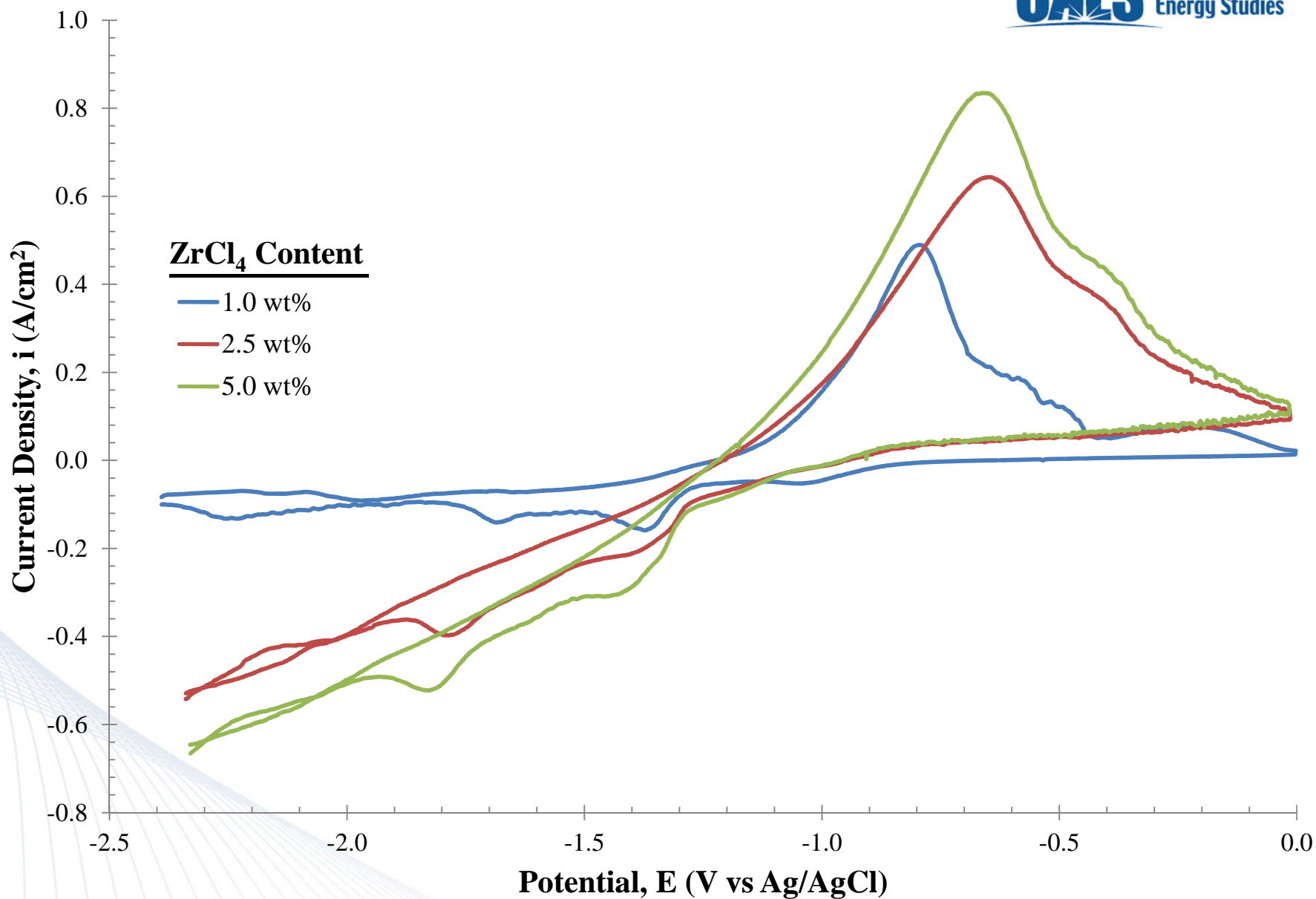
Cyclic Voltammogram (2.5 wt% ZrCl_4)



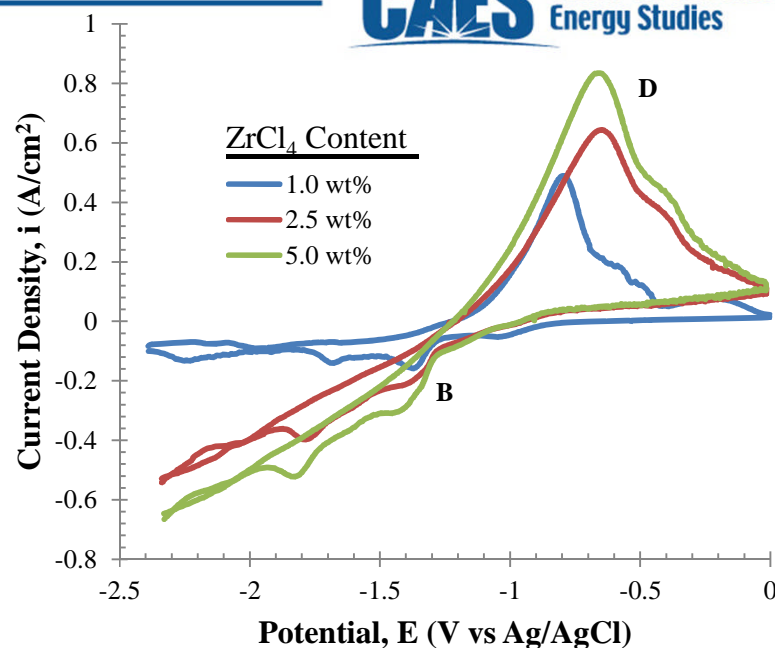
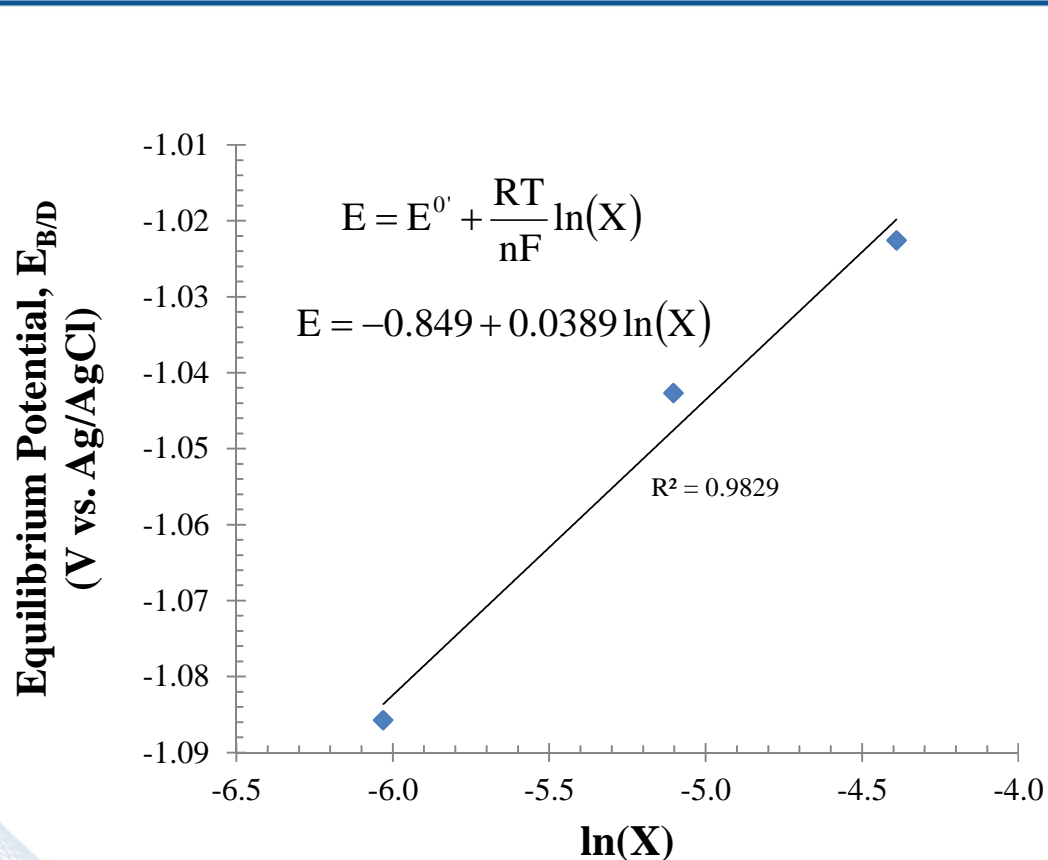
Cyclic Voltammogram (5.0 wt% ZrCl_4)



Cyclic Voltammogram Comparison

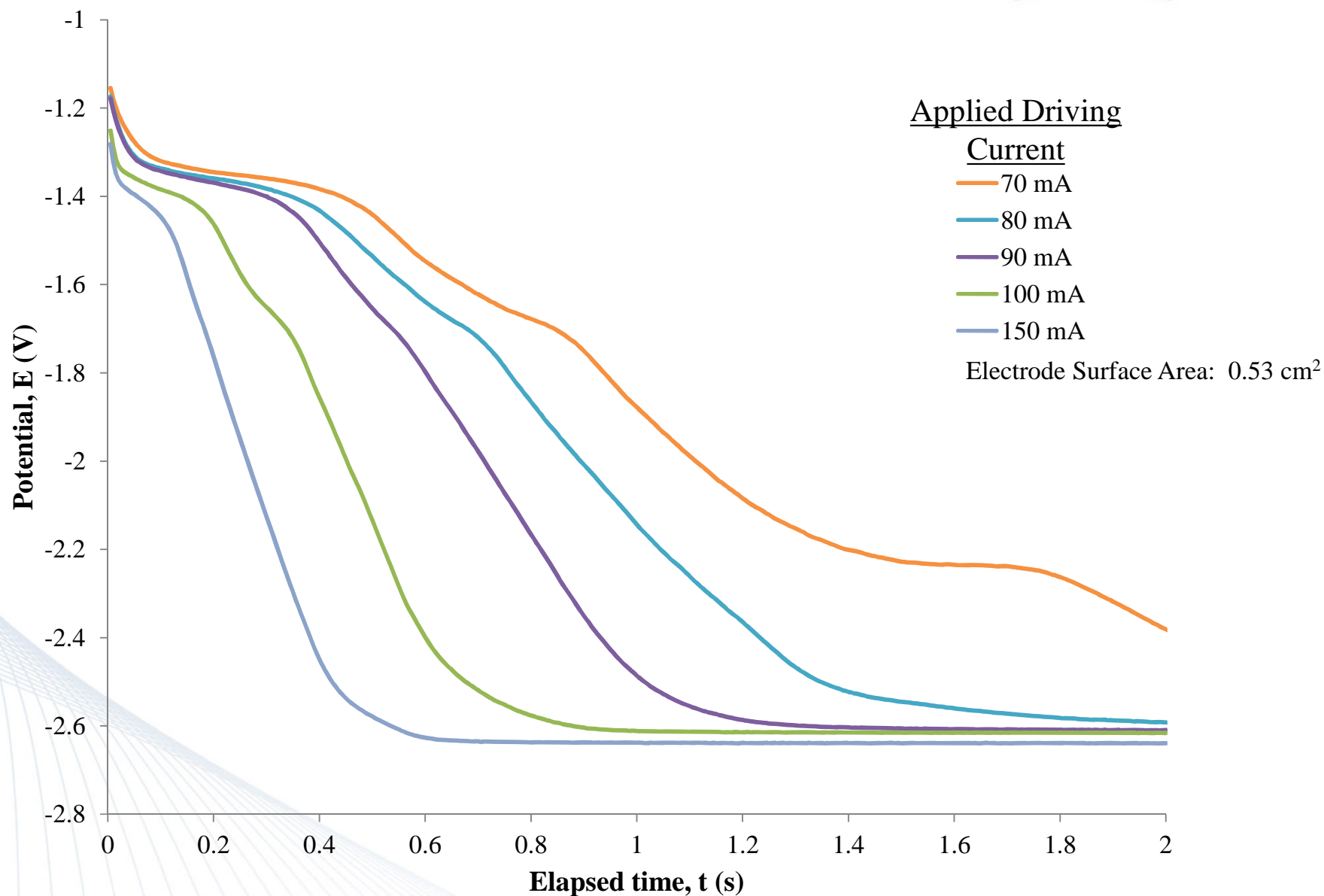


Nernst Plot for Peaks B and D



- Apparent reduction potential:
 $E^{0'} = -0.849$ V (vs Ag/AgCl)
- Average number of electrons transferred in the reaction(s):
 $n = 1.71$

Chronopotentiometry (1.0 wt% ZrCl_4)



Summary

- An experimental setup and process has been designed to test properties relevant to the electrochemical recovery of zirconium in molten salt.
- Cyclic voltammetry has been performed on (1.0, 2.5, and 5.0) wt% ZrCl_4 in the molten LiCl/KCl eutectic salt at 500 °C.
 - Cyclic voltammograms show complex behavior of zirconium in the molten salt with presence of ZrCl_4 , ZrCl_2 , and ZrCl .
 - Range of diffusion coefficients in the LiCl/KCl eutectic was determined.
 - $D = 2.37 \times 10^{-7} - 1.48 \times 10^{-4} \text{ cm}^2/\text{s}$
 - Apparent standard reduction potential was determined for one pair of peaks.
 - $E^{0'} = -0.849 \text{ V vs. Ag/AgCl}$
- Chronopotentiometry was performed and shows complex behavior.

Summary

	Standard Reduction Potential, E^0 (V vs. Ag/AgCl)			Diffusion Coefficient, D (m ² /s)		Activity Coefficient, γ	
	Zr(IV)/Zr	Zr(IV)/Zr(II)	Zr(II)/Zr	Zr(IV)	Zr(II)	Zr(IV)	Zr(II)
[2]	-1.22*	---	-1.12	---	---	9.6×10^{-6} *	3.4×10^7
[3]	-1.064*	-1.121*	-1.01*	---	---	---	---
[4]	-0.838	---	-0.722	---	---	3.081×10^{-3} *	1.05×10^{-4} *
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[6]	-1.333*	---	---	---	---	---	---
[7]	-1.1	---	---	---	---	---	---
[8]	-1.22	---	---	---	---	---	---
[9]	---	---	---	---	---	4.48×10^{-3}	1.9×10^{-4}
[10]	---	---	---	1.13×10^{-5}	---	---	---
[11]	---	---	---	$1.10 \times 10^{-7} - 4.53 \times 10^{-6}$		---	---
This Work	-0.849 (Effective)			$2.37 \times 10^{-7} - 1.48 \times 10^{-4}$			

* Values reported are at 450 ° C.

[2] R. Baboian, et al., *J. Electrochem. Soc.*, **112.12** (1965).

[3] J.A. Plambeck, *J. of Chemical and Engineering Data*, **12(1)** (1967).

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[9] R.K. Ahluwalia, et al., *Nucl. Tech.*, **133** (2001).

[10] D. Yamada, et al., *J. Alloys and Compounds*, **444-445** (2007).

Future Work

- Further analysis of chronopotentiometry data.
- Further work with ZrCl_4 at additional concentrations.
- Zirconium electrodeposition experiments with transparent setup to analyze zirconium deposit morphology.
- Experiments to optimize/maximize zirconium recovery.
 - Cathode material, operating temperature, applied potential.
- Electrochemistry experiments/analysis with UCl_3 in LiCl/KCl eutectic.
- Final phase of this work will explore the electrochemical recovery of zirconium in the presence of uranium.

Acknowledgements

- This work was performed as part of I-NERI Project 2010-001-K in conjunction with Seoul National University and Korea Atomic Energy Research Institute.
- Thanks to all those who have helped with this project including Debbie Lacroix, Sean Martin, Ammon Williams, Josh Versey, Mike Pack, Cindy Hanson, and Dalsung Yoon.

Thanks!



Activity Coefficient

- Nernst Equation

$$E = E^0 + \frac{RT}{nF} \ln(\gamma X_s)$$

- What is the activity coefficient, γ ?

- A factor included in order to take account of deviations from solution ideality in the liquid phase.
- It is related to the excess Gibbs energy, G^E , the difference between the actual and ideal Gibbs energy of a solution.

$$\overline{G}^E = RT \ln \gamma$$

G^E Excess Gibbs energy

- It is defined as a ratio of the fugacity of the species in solution and its mass fraction in solution times its pure species fugacity.

$$\gamma \equiv \frac{\hat{f}}{x f}$$

\hat{f} Fugacity in solution
 x Mass fraction in solution
 f Fugacity of pure species